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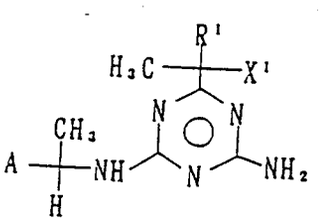
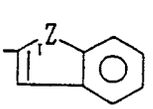
(54) **Herbicidal compositions.**

(57) A synergistic herbicidal composition comprising as active ingredients triazine derivatives represented by general formula [I]:



[wherein A represents



(wherein Z' represents oxygen atom or sulfur atom), or

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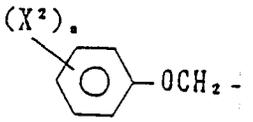
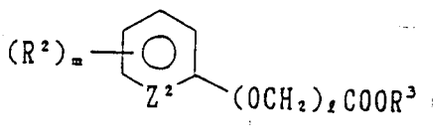


(wherein X^2 represents methyl group or fluorine atom and n represents 0 or an integer of 1 or 2); R^1 represents hydrogen atom or methyl group; and X^1 represents fluorine atom or chlorine atom] and a compound represented by general formula [II]:



wherein Z^2 represents a nitrogen atom or CH, R^2 represents a fluorine atom, a chlorine atom, methyl group, methoxy group or amino group, R^3 represents a hydrogen atom, methyl group, NH_4, an alkali metal or $NH(CH_3)_2$, m represents an integer of 1 to 4 and ℓ represents 0 or 1].

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to a herbicidal composition comprising triazine derivatives and specific compounds as active ingredients.

STATEMENT OF THE PRIOR ART

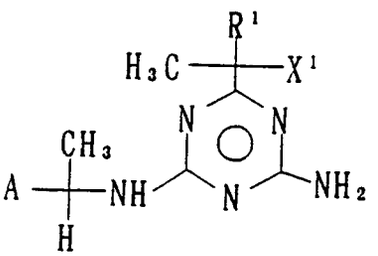
Heretofore a variety of herbicides have been developed and have contributed to agricultural productivity and saving labors. However, some herbicides have been used over many years and hence, weeds which are insufficiently controlled are increasing. It has thus been desired to develop herbicides having a wide range of herbicidal spectrum and those effective also against such troublesome weeds. Also in order to remove environmental pollution problems caused by conventional berbicides, it has been desired to develop berbicides having a high activity at a low dosage. Moreover, in order to control weeds emerging non-uniformly over a long period of time, it has been desired to develop herbicides having an excellent residual activities and having flexibility of treatment to exhibit effectiveness even though the treatment is performed over a long period from preemergence to a wide range of growing stage of weeds.

Under such a situation, the present inventors found that specific, novel triazine derivatives containing a halo alkyl are compounds which show a high herbicidal effect against troublesome weeds both by soil treatment and by foliage treatment, without causing any phytotoxicities of Gramineae field crops, and moreover provide an excellent effectiveness against weeds in paddy fields (Japanese Patent Application Nos. 1-38178 and 1-154465). The present inventors made extensive investigations to further improve the herbicidal activity of the triazine derivatives.

As a result, it has been found that a composition comprising the triazine derivatives in combination with specific compounds exhibit excellent herbicidal activity which can be unexpected from each property of these compounds and shows a high herbicidal effect at a low dosage and at the same time, has a wide range of herbicidal spectrum. The present invention has thus been accomplished.

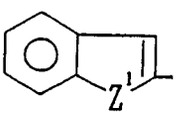
SUMMARY OF THE INVENTION

That is, the present invention provides a herbicidal composition comprising as active ingredients triazine derivatives represented by general formula [I]:

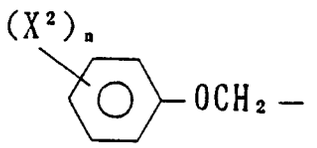


... [I]

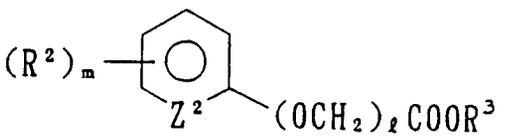
[wherein A represents



(wherein Z^1 represents oxygen atom or sulfur atom), or



(wherein X^2 represents methyl group or fluorine atom and n represents 0 or an integer of 1 or 2); R^1 represents hydrogen atom or methyl group; and X^1 represents fluorine atom or chlorine atom] and a compound represented by general formula [II]:

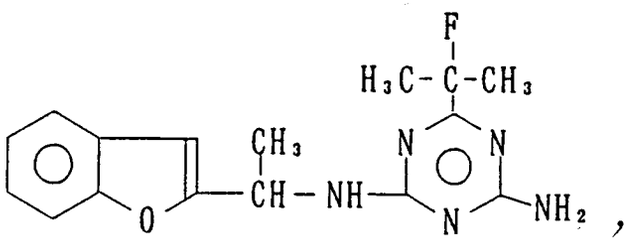


… [II]

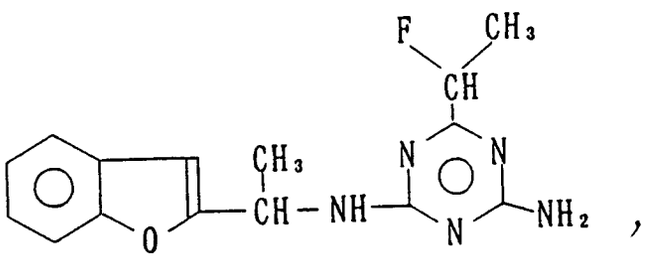
[wherein Z^2 represents a nitrogen atom or CH, R^2 represents a fluorine atom, a chlorine atom, methyl group, methoxy group or amino group, R^3 represents a hydrogen atom , methyl group, NH_4, an alkali metal or NH-$(CH_3)_2$, m represents an integer of 1 to 4 and ℓ represents 0 or 1].

DETAILED DESCRIPTION OF THE INVENTION

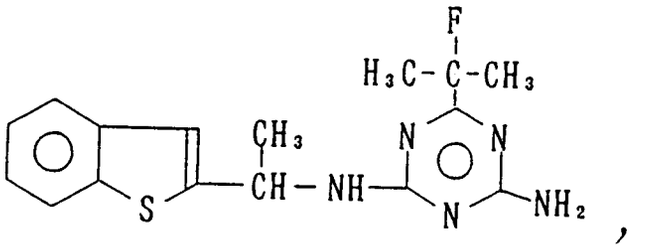
Specific examples of the triazine derivatives represented by general formula [I] described above include: 2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6-(α-fluoro, α-methylethyl)-s-triazine



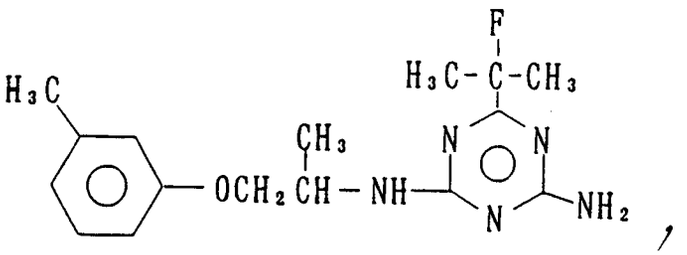
2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6-(α-fluoroethyl)-s-triazine



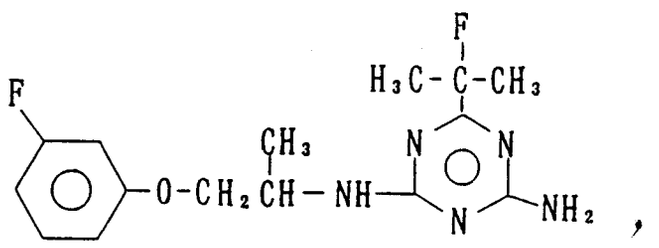
2-amino-4-[1-(benzothiophen-2'-yl)ethylamino]-6-(α-fluoro, α-methylethyl)-s-triazine



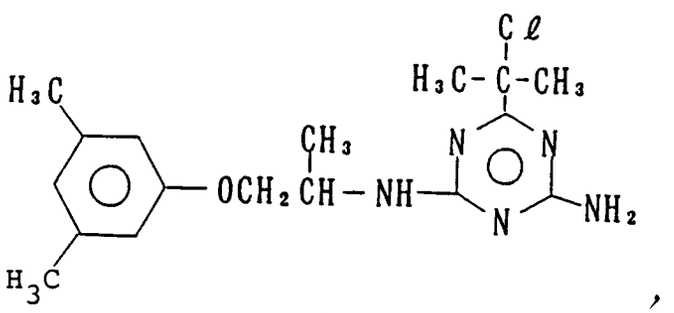
2-amino-4-(α-fluoro, α-methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine



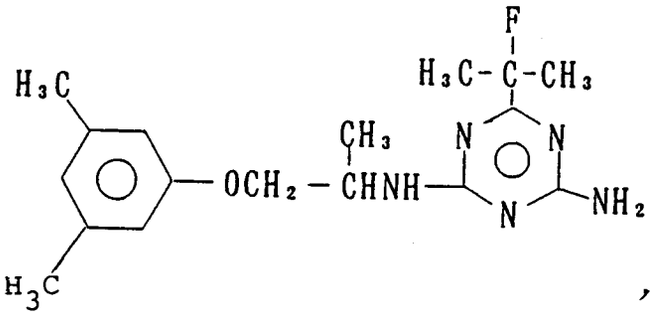
2-amino-4-(α-fluoro, α-methylethyl)-6-[2-(3'fluorophenoxy)-1-methylethylamino]-s-triazine



2-amino-4-(α-chloro, α-methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine



2-amino-4-(α-fluoro, α-methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine

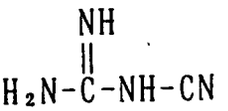


etc.

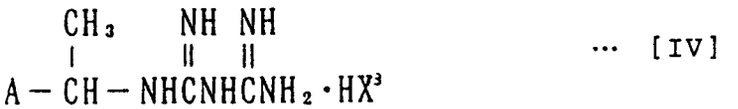
The triazine derivatives represented by general formula [I] described above may be prepared by various processes. Among these processes, an advantageous process comprises reacting alkyl amine salts represented by general formula [III]:

... [III]

[wherein A has the same significance as described above and X^3 represents a halogen atom] with cyanoguanidine represented by the following formula:

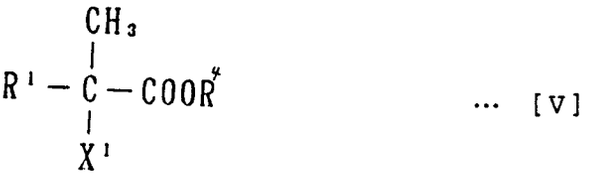


to prepare alkyl biguanide salts represented by general formula [IV]:



... [IV]

[wherein A and X^3 have the same significances as described above]; and then reacting the alkyl biguanide salts with alkyl esters represented by general formula [V]:



... [V]

[wherein R^1 and X^1 have the same significances as described above; and R^4 represents an alkyl group having 1 to 4 carbon atom]. According to this process, the desired triazine derivatives represented by general formula [I] can be efficiently obtained by reacting the alkylamine salts represented by general formula [III] with cyanoguanidine to prepare the alkyl biguanide salts represented by general formula [IV], and then reacting the salts [IV] with the alkyl esters represented by general formula [V].

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein, in the reaction of the alkylamine salts represented by general formula [III] with cyanoguanidine, both compounds may be used in equimolar amounts. As a solvents, there may be used cyclic hydrocarbons such as benzene, decaline, alkylnaphthalenes, etc.; chlorinated hydrocarbons such as carbon tetrachloride, ethylene dichloride, chlorobenzene, dichlorobenzene, trichlorobenzen, etc. A reaction temperature is not particularly limited but the reaction sufficiently proceeds at a high temperature ranging from 80 to 200 ° C.

According to this reaction, the alkylbiguanide derivative salts shown by general formula [IV] are obtained. By reacting [IV] with alkyl esters represented by general formula [V], the desired triazine derivatives represented by general formula [I] are prepared. This reaction efficiently proceeds generally in a solvent such as alcohols, e.g., methanol, ethanol, isopropanol, etc., various ketones, aliphatic hydrocarbons, various ethers, various cyclic hydrocarbons, chlorinated hydrocarbons, etc., in the presence of a catalyst such as a base, etc. at a temperature of about 10 to about 100 ° C.

Optical isomers are also present in these compounds and the products are obtained generally in the racemic form. However, it is also possible to the respective enantiomers in a conventional manner such as asymmetric synthesis, etc. In the present invention, both racemic compounds and optical isomers alone may be used. In the present invention, the products may be in the form of salts with inorganic acid or organic acid.

On the other hand, specific examples of the compound represented by general formula [II] described above include 2,3,6-trichlorobenzoic acid; 3,6-dichloro-2-methoxybenzoic acid; 3-amino-2,5-dichlorobenzoic acid; 2,3,5-trichloro-6-methoxybenzoic acid; 4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid; 3,6-dichloro-2-pyridinecarboxylic acid; (3,5,6-trichloro-2-pyridinyl)-oxyacetic acid; (4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxyacetic acid, etc. Among them, preferred are 3,6-dichloro-2-methoxybenzoic acid and (4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxyacetic acid.

The compounds represented by general formula [II] can be prepared by known process. These compounds have a spectrum for broad-leaved weeds and are used for crops of corn, wheat, barley, etc. or also in non-cultivated field, etc.

The herbicidal composition of the present invention comprises as active ingredients the triazine derivatives represented by general formula [I] described above and the compounds represented by general formula [II] described above. A proportion of these components to be formulated is not particularly limited but in a wide range of proportion, an excellent synergistic effect can be obtained. In general, it is preferred to formulate the triazine derivative and the compounds represented by general formula [II] in a range of from 10 : 1 to 1 : 100 (weight ratio).

The herbicidal composition of the present invention may be used in the form of wettable powders, emulsifiable concentrates, dusts, granules, flowable concentrates, solutions, etc., by blending the triazine derivatives represented by general formula [I] described above and the compounds represented by general formula [II] described above with liquid carriers such as solvents, etc. or with solid carriers such as mineral powders, etc. In preparing into these forms, there may be added surfactants such as emulsifiers, dispersing agents, developers, suspending agents, permeating agents, stabilizers, etc. and, if necessary, other auxiliary agents.

Where the herbicidal composition of the present invention is used in the form of wettable powders, 10 to 55 wt% of the aforesaid triazine derivatives and the compounds represented by general formula [II] as active ingredients, 40 to 88 wt% of the solid carrier and 2 to 5 wt% of the surfactant may generally be formulated to prepare a composition and the composition may be used. Where the herbicidal composition is used in the form of emulsifiable concentrate or flowable concentrate, 5 to 50 wt% of the aforesaid triazine derivatives and the compounds represented by general formula [II] as active ingredients, 35 to 90 wt% of the solvent and 5 to 15 wt% of the surfactant and other auxiliary agent may generally be formulated to prepare a composition and the resulting composition may be used.

Where herbicidal composition is used in the form of dust, 1 to 15 wt% of the aforesaid triazine derivatives and the compounds represented by general formula [II] as active ingredients and 85 to 99 wt% of the solid carrier may generally be formulated to prepare a composition. Where the herbicidal composition of the present invention is used in the form of granules, 0.1 to 15 wt% of the aforesaid triazine derivatives and the compounds represented by general formula [II] as active ingredients, 80 to 97.9 wt% of the solid carrier and 2 to 5 wt% of the surfactant may generally be formulated to prepare a composition. Herein, as the solid carrier, finely divided mineral powders are used. As the finely divided mineral powders, there are diatomaceous earth, oxides such as slaked lime, etc.; phosphates such as apatite, etc.; sulfates such as gypsum, etc.; silicates such as talc, pyrophyllite, clay, kaolin, bentonite, acid clay, white carbon, quartz

powders, silica powders, etc.

As the liquid carrier, there may be organic solvents, for example, paraffin type or naphthene type hydrocarbons such as kerosene, mineral oil, spindle oil, etc.; aromatic hydrocarbons such as benzene, toluene, xylene, etc.; chlorinated hydrocarbons such as o-chlorotoluene, trichloromethane, trichloroethylene, etc.; alcohols such as cyclohexanol, amyl alcohol, ethylene glycol, etc.; alcohol ethers such as ethylene glycol monomethyl ether, ethylenen glycol monoethyl ether, etc.; ketones such as isophorone, cyclohexanone, cyclohexenyl-cyclohexanone, etc.; ethers such as butyl cellosolve, dimethyl ether, methyl ethyl ether, etc.; esters such as isopropyl acetate, benzyl acetate, methyl phthalate, etc.; amides such as dimethylformamide, etc.; nitriles such as acetonitrile, propionitrile, etc.; sulfoxides such as dimethylsulfoxide, etc.; or a mixture thereof; or water and the like.

As the surfactant, there may be used any of anion type (alkylbenzene sulfonate, alkyl sulfonates, laurinamide sulfonate, etc.), nonion type (polyoxyethylene octyl ether, polyethylene glycol laurate, sorbitan alkyl esters, etc.), cation type (dimethyllaurylbenzyl ammonium chloride, laurylamine, stearyltrimethyl ammonium chloride, etc.) and amphoteric type (amino acids, betaine, etc.).

For purposes of improving properties of the preparation and enhancing the herbicidal effect, the herbicidal composition of the present invention may also contain high molecular compounds such as sodium alginate, carboxymethyl cellulose, carboxyvinyl polymer, gum arabic, hydroxypropylmethyl cellulose, etc. and auxiliary agents in combination.

The herbicidal composition of the present invention exhibits an excellent effect on weeds in field crops such as corn, sorghum, wheat, barley, oat, etc., as a high degree of selective herbicide without causing any phytotoxicities to crops by pre- or post-emergence treatment to the soil or the foliage of weeds. The herbicidal composition shows a high herbicidal effect not only against annual weeds but also against perennial weeds and also exhibits an excellent effect of controlling weeds in orchards or non-cultivated fields (factory areas, railways, roadsides, waterways, fallow grounds), etc., by treatment to the soil or to the foliage of weeds.

The herbicidal composition of the present invention is applied in an amount of about 0.1 to 10,000 g, preferably 1 to 1,000 g, per 10 ares. Where the composition is sprayed over the foliage of plant, the composition is diluted to about 1 to about 100,000 ppm, preferably 10 to 10,000 ppm and the diluted preparation is applied to the foliage.

The herbicidal composition of the present invention may also be used in combination with other herbicids. Examples of the conventional herbicids which can be used herein include diphenyl ether compounds, triazine compounds, phenoxyacetic acid compounds, carbamate compounds, thiocarbamate compounds, acid anilide compounds, pyrazole compounds, phosphoric acid compounds, sulfonylurea compounds, imidazolinone compounds, dinitroaniline compounds, bromoxinyl, ioxinyl, oxadiazone, etc.

Furthermore, the herbicidal composition of the present invention may also be used as admixture with insecticides, sterilizers, plant growth regulators, fertilizers, etc., if necessary.

Next, the present invention is described with reference to examples.

Firstly, a method for making formulations is specifically described by referring to formulation examples. In the following formulation examples, "part" refers to % by weight. As the triazine derivative (Compound A) and the compound represented by general formula [II](Compound B) compounds shown in Tables 1 and 2 were used, respectively.

Table 1

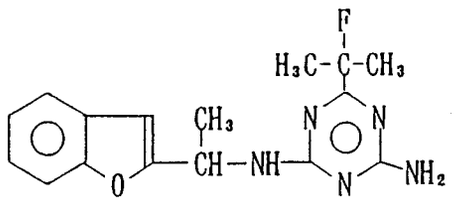
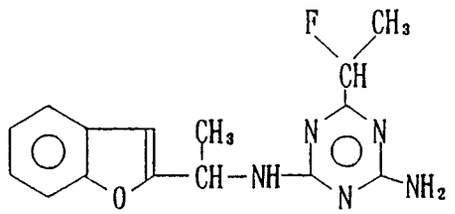
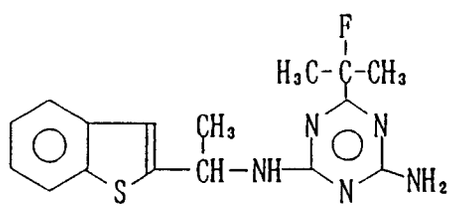
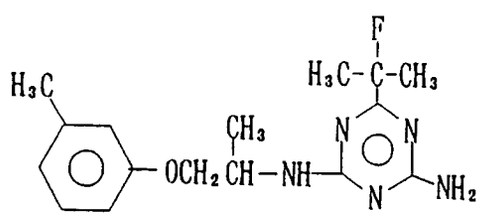
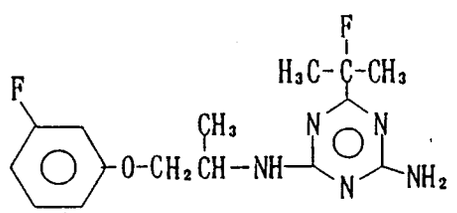
Compound No.	Structural Formula	Name of Compound
A-1		2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6-(α-fluoro, α-methylethyl)-s-triazine
A-2		2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6(α-fluoroethyl)-s-triazine
A-3		2-amino-4-[1-(benzothiophen-2'-yl)ethylamino]-6-(α-fluoro,α-methylethyl)-s-triazine
A-4		2-amino-4-[α-fluoro,α-methylethyl-6-(2-3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine
A-5		2-amino-4-(α-fluoro,α-methylethyl)-6-[2-(3'-fluorophenoxy)-1-methyl-ethylamino]-s-triazine

Table 1 (Continued)

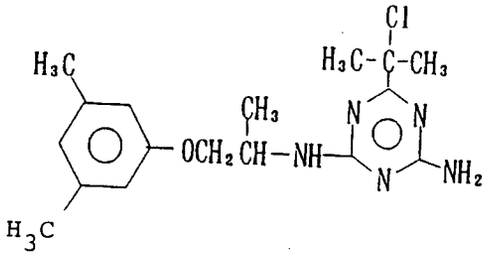
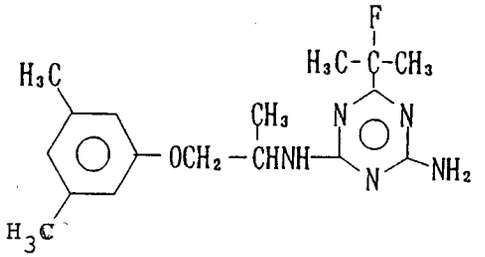
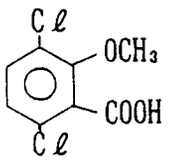
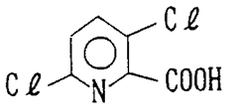
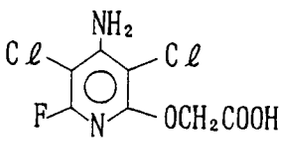
Compound No.	Structural Formula	Name of Compound
A-6		2-amino-4-(α-chloro,α-methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine
A-7		2-amino-4-(α-fluoro,α-methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine

Table 2

Compound No.	Structural Formula	Name of Compound
B-1		3,6-dichloro-2-methoxybenzoic acid
B-2		3,6-dichloro-2-pyridinecarboxylic acid
B-3		(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)-oxyacetic acid

Formulation Example 1 Wettable powders

Compound A-1	5 parts
Compound B-1	15 parts
Diatomaceous earth	62 parts
White carbon	15 parts
Sodium alkylbenzenesulfonate	2 parts
Sodium lignin sulfonate	1 part

The foregoing components are blended with each other, uniformly kneaded and ground into powders to give 100 parts of wettable powders.

Formulation Example 2 Emulsifiable concentrate

Compound A-2	10 parts
Compound B-2	30 parts
Xylene	20 parts
Dimethylformamide	20 parts
Solpol 2806B (manufactured by Toho Chemical Industry, surfactant)	20 parts

The foregoing components are uniformly dissolved and blended to give 100 parts of emulsifiable concentrate.

Formulation Example 3 Dust

Compound A-3	0.6 part
Compound B-3	1.4 parts
Diatomaceous earth	20 parts
Talc	78 parts

The foregoing components are blended with each other, uniformly kneaded and ground to give 100 parts of dusts.

Formulation Example 4 Granule

Compound A-5	1 part
Compound B-2	3 parts
Bentonite	30 parts
Talc	63 parts
Sodium lignin sulfonate	3 parts

The foregoing components are thoroughly blended with each other, uniformly mixed and ground into powders. Water is added to the powders. After kneading them well, the blend is grained and dried to give 100 parts of granules.

Formulation Example 5 Flowable concentrate

Compound A-7	10 parts
Compound B-3	15 parts
Methyl cellulose	0.3 part
Colloidal silica	1.5 parts
Sodium lignin sulfonate	1 part
Polyoxyethylene nonyl phenyl ether	2 parts
Water	70.2 parts

The foregoing components are thoroughly mixed and dispersed. The resulting slurry mixture is subjected to wet grinding to give 100 parts of stable flowable concentrate. Formulation Example 6 - Wettable powders

By uniformly blending 97 parts of clay (trademark: JIKURAITO, manufactured by JIKURAITO KOGYO) as a carrier, 1.5 parts of alkylaryl sulfonate (trademark: NEOPELEX, manufactured by Kao Atlas Co., Ltd.) as a surfactant, 1.5 parts of nonionic and anionic surfactant (trademark: Solpol 800A, manufactured by Toho Chemical Industry Co., Ltd.) and grinding into powders, a carrier for wettable powders was obtained.

By uniformly blending 90 parts of this carrier for wettable powders and 10 parts of the triazine derivative shown in Table 1 (Compounds A-1 through A-7) or 10 parts of the compounds shown in Table 2 (Compounds B-1 to B-3) and grinding into powders, wettable powders were obtained.

Furthermore, the carrier for wettable powders containing the triazine derivative obtained above was blended with the carrier for wettable powders containing the compounds shown in Table 2 in definite amounts (ratios as active ingredients), uniformly kneaded and ground into powders to give wettable powders.

Example 1 Test on post-emergence treatment

Wagner's pots of 1/2000 ares were filled with soil from upland fields and planted with weed seeds of Abutilon theophrasti, Ipomoea purpurea, Galium aparine L. and Viola arvensis and crop seeds of corn, sorghum, wheat, barley and oat. The seeds were then covered with soil and cultivated in a greenhouse. An aqueous suspension of a definite amount of the herbicide obtained in Formulation Example 6 was uniformly sprayed onto the foliage of 1.5 to 2.5 leaf stage of these weeds and 3 leaf stage of the crops at a spray volume corresponding to 100 liters/10 ares. Then, cultivation was performed in the greenhouse. After 20 days, crop injury and the herbicidal effect on the weeds were evaluated according to the criterion described below. The results are shown in Table 3.

(Criterion for assessment)

Degree of herbicidal effect	Percent of weed control (herbicidal rate)
0	less than 5% (little effective)
1	5-20%
2	20-40%
3	40-70%
4	70-80%
5	more than 90% (almost all killed)

The herbicidal rate described above was determined according to the following equation by measuring the raw weight of weed on the ground in the treated group and the raw weight of weed on the ground in the untreated group.

$$\text{Herbicidal rate (\%)} = \left(1 - \frac{\text{Weight of weed on the ground in the treated group}}{\text{Weight of weed on the ground in the untreated group}}\right) \times 100$$

Degree of crop injury

0 no injury to crops
1 little injury to crops
2 some injury to crops
3 injury to crops
4 serious injury to crops
5 almost all crops are withered to death

Table 3

Active ingredient		Dosage (g/10a)	Herbicidal Effect				Crop Injury			
			Abutilon theophrasti	Ipomoea purpurea	Galium aparine L.	Viola arvensis	Corn	Sorghum	Wheat	Barley
Triazine Derivative	A-1	10	3	4	2	3	0	0	0	0
		5	1	2	1	2	0	0	0	0
	A-2	10	4	4	3	4	0	0	0	0
		5	2	3	1	3	0	0	0	0
	A-3	10	3	4	2	3	0	0	0	0
		5	2	2	1	2	0	0	0	0
	A-4	10	3	4	3	4	0	0	0	0
		5	2	3	1	2	0	0	0	0
	A-5	10	4	5	3	4	0	0	0	0
		5	3	4	2	3	0	0	0	0
	A-6	10	3	5	3	4	0	0	0	0
		5	2	3	1	2	0	0	0	0
	A-7	10	4	5	3	4	0	0	0	0
		5	3	4	2	3	0	0	0	0
Compound represented by general formula [I1]	B-1	10	3	3	3	2	0	0	0	0
		5	2	2	2	1	0	0	0	0
	B-2	10	3	3	2	3	0	0	0	0
		5	2	1	1	1	0	0	0	0
	B-3	15	3	3	4	3	0	0	0	0
		10	1	2	3	2	0	0	0	0

Table 3 (Continued)

Triazine Derivative		Compound represented by general formula [II]		Herbicidal Effect				Crop Injury			
Kind	Dosage (g/10a)	Kind	Dosage (g/10a)	Abutilon theophrasti	Ipomoea purpurea	Galium aparine L.	Viola arvensis	Corn	Sorghum	Wheat	Barley
A1	10	B1	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A1	10	B3	15	5	5	5	5	0	0	0	0
	10		10	5	5	5	5	0	0	0	0
	5		15	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
A2	10	B1	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A2	10	B2	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A2	10	B3	15	5	5	5	5	0	0	0	0
	10		10	5	5	5	5	0	0	0	0
	5		15	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
A3	10	B1	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A3	10	B3	15	5	5	5	5	0	0	0	0
	10		10	5	5	5	5	0	0	0	0
	5		15	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
A4	10	B1	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A4	10	B3	15	5	5	5	5	0	0	0	0
	10		10	5	5	5	5	0	0	0	0
	5		15	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0

Table 3 (Continued)

Triazine Derivative		Compound represented by general formula [II]		Herbicidal Effect				Crop Injury			
Kind	Dosage (g/10a)	Kind	Dosage (g/10a)	Abutilon theophrasti	Ipomoea purpurea	Galium aparine L.	Viola arvensis	Corn	Sorghum	Wheat	Barley
A5	10	B1	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A5	10	B2	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A5	10	B3	15	5	5	5	5	0	0	0	0
	10		10	5	5	5	5	0	0	0	0
	5		15	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
A6	10	B1	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A6	10	B3	15	5	5	5	5	0	0	0	0
	10		10	5	5	5	5	0	0	0	0
	5		15	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
A7	10	B1	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A7	10	B2	10	5	5	5	5	0	0	0	0
	10		5	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0
	5		5	5	5	5	5	0	0	0	0
A7	10	B3	15	5	5	5	5	0	0	0	0
	10		10	5	5	5	5	0	0	0	0
	5		15	5	5	5	5	0	0	0	0
	5		10	5	5	5	5	0	0	0	0

Some data were extracted from the results shown in Table 3 and the synergistic effect of the triazine derivative and the compounds represented by general formula [II] was examined on Ipomoea purpurea and Viola arvensis according to the following method.

$$Q\,E = Q\,a + Q\,b - \frac{Q\,a \cdot Q\,b}{1\,0\,0}$$

Q a : found data (%) of herbicidal rate when treated at a dosage corresponding to a g/10 ares using the triazine derivative alone as active ingredient

Q b : found data (%) of herbicidal rate when treated at a dosage corresponding to b g/10 ares using the compound represented by general formula [II] alone as active ingredient

Q E : expected value

[Limpel, L.E., P.H. Schuldt and D. Lamont, Proc. NEWCC, 16, 48-53 (1962)]

Herein, when the found data (herbicidal rate) of the herbicidal obtained by mixing the triazine derivative and the compounds represented by general formula [II] is larger than Q E, it can be said that the herbicidal activity is synergistic. The results are shown in Table 4.

Table 4

Triazine Derivative		Compound represented by general formula [II]		Herbicidal Effect			
Kind	Dosage (g/10a)	Kind	Dosage (g/10a)	Percent control of Ipomoea purpurea (%)	Expected Value (Q_E)(%)	Percent control of Viola arvensis (%)	Expected Value (Q_E)(%)
-	-	B1	10	60	-	38	-
-	-	B2	10	58	-	64	-
-	-	B3	15	64	-	68	-
A1	5	-	-	36	-	38	-
A1	5	B1	10	92	74	90	62
A1	5	-	-	36	-	38	-
A1	5	B3	15	93	77	95	80
A2	5	-	-	58	-	64	-
A2	5	B1	10	94	83	93	78
A2	5	-	-	58	-	64	-
A2	5	B2	10	96	82	94	87
A2	5	-	-	58	-	64	-
A2	5	B3	15	92	85	98	88
A3	10	-	-	72	-	62	-
A3	10	B1	10	100	89	92	76
A3	10	-	-	72	-	62	-
A3	10	B3	15	99	90	94	88
A4	5	-	-	52	-	38	-
A4	5	B1	10	97	81	90	62
A4	5	-	-	52	-	38	-
A4	5	B3	15	94	83	92	80
A5	5	-	-	72	-	68	-
A5	5	B1	10	95	89	97	80
A5	5	-	-	72	-	68	-
A5	5	B2	10	96	88	99	88
A5	5	-	-	72	-	68	-
A5	5	B3	15	94	90	100	90
A6	5	-	-	63	-	36	-
A6	5	B1	10	93	85	90	60
A6	5	-	-	63	-	36	-
A6	5	B3	15	95	87	92	80
A7	5	-	-	70	-	58	-
A7	5	B1	10	98	88	94	74
A7	5	-	-	70	-	58	-
A7	5	B2	10	97	87	94	85
A7	5	-	-	70	-	58	-
A7	5	B3	15	100	89	93	87

Example 2 Field test (post-emergence treatment test)

Test zone having each plot of 2 m^2 were prepared and weed seeds of Xanthium strumarium, Ipomoea purpurea, Abutilon theophrasti, Portulaca oleracea, Solanum nigrum, Cassia obtusifolia L., and Amaranthus retroflexus and crop seeds of corn and sorghum were simultaneously planted.

When weeds grew at the 2-3 leaf stage and corn and sorghum reached the 3-leaf stage, a given amount of a dilution of the herbicide obtained in Formulation Example 6 was uniformly sprayed onto the foliage at a spray volume corresponding to 20 liters/10 ares. The test was carried out by 3 replications.

The weeds on the ground which survived 30 days after spraying of the chemical were cut out and their raw weights were measured. According to the following equation, a weed controlling rate was determined as an average of the 3 replicates.

$$\text{Percent of weed control (\%)} = \left(1 - \frac{\text{Weight of survived weed on the ground in the treated plot}}{\text{Weight of survived weed on the ground in the untreated plot}}\right) \times 100$$

With respect to wheat and barley, their raw weights on the ground were measured also as in weeds and the degree of crop injury (inhibition rate) was determined. The results are shown in Table 5.

Table 5

Active ingredient	A2 + B1		A7 + B1	
Dosage(g/10a)	20+20	10+20	20+20	10+20
Percent of Weed Control(%)				
Xanthium strumarium	100	100	100	100
Ipomoea purpurea	100	100	100	100
Abutilon theophrasti	100	100	100	100
Portulaca oleracea	100	100	100	100
Solanum nigrum	100	100	100	100
Cassia obtusifolia L.	100	100	100	100
Amaranthus retroflexus	100	100	100	100
Crop Injury				
Corn	0	0	0	0
Sorghum	0	0	0	0

Example 3 Field test (post-emergence treatment test)

Test zone having each plot of 2 m^2 were prepared and weed seeds of Galium aparine L., Stellaria media, Viola arvensis, Matricaria inodora, Veronica hedelifolia, Papaver rhoeas and Aphanes arvensis and crop seeds of wheat and barley were simultaneously planted.

When weeds grew at the 2-3 leaf stage and wheat and barley reached the 3-leaf stage, a given amount of a dilution of the herbicide obtained in Formulation Example 6 was uniformly sprayed onto the foliage at a spray volume corresponding to 20 liters/10 ares. The test was carried out by 3 replications.

The percent of weed control and the degree of crop injury were determined 30 days after spraying the chemical in a manner similar to Example 2. The results are shown in Table 6.

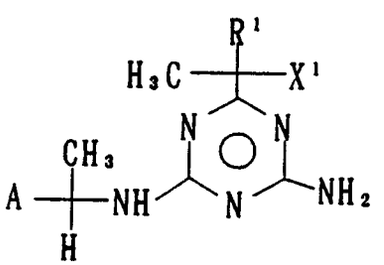
Table 6

Active ingredient	A2 + B3		A7 + B3	
Dosage(g/10a)	20+15	10+15	20+15	10+15
Percent of Weed Control(%)				
Galium aparine L.	100	100	100	100
Stellaria media	100	100	100	100
Viola arvensis	100	100	100	100
Matricaria inodora	100	100	100	100
Veronica hedelifolia	100	100	100	100
Papaver rhoeas	100	100	100	100
Aphanes arvensis	100	100	100	100
Crop Injury				
Wheat	0	0	0	0
Barley	0	0	0	0

By the synergistic effect of the triazine derivative and compounds represented by general formula [II] as active ingredient, the herbicidal composition of the present invention show a high herbicidal effect at a low dosage and also have a wide range of herbicidal spectrum. Further when the composition is used as herbicide for field crops, the composition has flexibility of treatment to exhibit effectiveness, as compared to in conventional herbicides for field crops. The composition also shows a high herbicidal activity even against troublesome weeds both by treatment to the soil at the pre- or post-emergence of weeds and by treatment to the foliage at the post-emergence of weeds. In addition, no crop injury is caused. In particular, the effect is markedly high in treatment to the soil or foliage treatment in fields where Gramineae crops grow. While the invention has been described in detail and with reference to specific embodiments thereof, it is apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and the scope of the present invention.

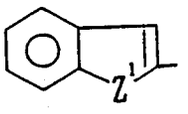
Claims

1. A herbicidal composition comprising as active ingredients a triazine derivative represented by general formula [I]:

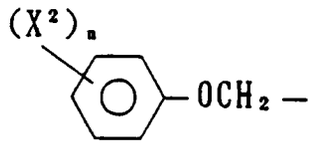


... [I]

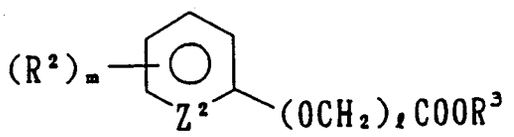
wherein A represents



wherein Z^1 represents oxygen atom or sulfur atom, or



wherein X^2 represents methyl group or fluorine atom and n represents 0 or an integer of 1 or 2; R^1 represents hydrogen atom or methyl group; and X^1 represents fluorine atom or chlorine atom and a compound represented by general formula [II]:



… [II]

wherein Z^2 represents a nitrogen atom or CH, R^2 represents a fluorine atom, a chlorine atom, methyl group, methoxy group or amino group, R^3 represents a hydrogen atom, methyl group, NH_4, an alkali metal or $NH(CH_3)_2$, m represents an integer of 1 to 4 and ℓ represents 0 or 1.

2. The herbicidal composition as claimed in claim 1,wherein the triazine derivative represented by general formula [I] is a triazine derivative selected from the group consisting of 2-amino-4-[1-(benzofuran-2'-yl)-ethylamino]-6-(α-fluoro, α-methylethyl)-s-triazine, 2-amino-4-[1-(benzofuran-2'-yl)ethylamino]-6-(α-fluoroethyl)-s-triazine, 2-amino-4-[1-(benzothiophen-2'-yl)ethylamino]-6-(α-fluoro, α-methylethyl)-s-triazine, 2-amino-4-(α-fluoro, α-methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine, 2-amino-4-(α-fluoro, α-methylethyl)-6-[2-(3'fluorophenoxy)-1-methylethylamino]-s-triazine, 2-amino-4-(α-chloro, α-methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine and 2-amino-4-(α-fluoro, α-methylethyl)-6-[2-(3',5'-dimethylphenoxy)-1-methylethylamino]-s-triazine.

3. The herbicidal composition as claimed in claim 1,wherein the compound represented by general formula [II] is a compound selected from the group consisting of 2,3,6-trichlorobenzoic acid; 3,6-dichloro-2-methoxybenzoic acid; 3-amino-2,5-dichlorobenzoic acid; 2,3,5-trichloro-6-methoxybenzoic acid; 4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid; 3,6-dichloro-2-pyridinecarboxylic acid; (3,5,6-trichloro-2-pyridinyl)-oxyacetic acid and (4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxyacetic acid.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 2099

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 932 998 (T. TAKEMATSU et al.) * Column 18, lines 40-51 *	1-3	A 01 N 43/68 // (A 01 N 43/68 A 01 N 43:40 A 01 N 39:04 A 01 N 37:44 A 01 N 37:40 A 01 N 37:10)
A,P	EP-A-0 411 153 (IDEMITSU KOSAN)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A 01 N

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	24 September 91	DECORTE D.

CATEGORY OF CITED DOCUMENTS

- X : particularly relevant if taken alone
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- A : technological background
- O : non-written disclosure
- P : intermediate document
- T : theory or principle underlying the invention
- E : earlier patent document, but published on, or after the filing date
- D : document cited in the application
- L : document cited for other reasons

& : member of the same patent family, corresponding document